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SEPARATION AND CHARACTERIZATION OF RU₂O₅(CO)₁₂ AND RUO₅2(CO)₁₂--ETC(U)
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(6) Separation and Characterization of $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$.
Experiments Pertaining to the Mechanism of the Cluster
Catalyzed Water Gas Shift Reaction.

by

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <table border="0"> <tr> <td>Clusters</td> <td>$\text{RuOs}_2(\text{CO})_{12}$</td> <td>$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$</td> <td>$\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$</td> </tr> <tr> <td>Catalysis</td> <td>$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$</td> <td>$\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$</td> <td>Mixed-metal clusters</td> </tr> <tr> <td>Water-Gas</td> <td></td> <td></td> <td></td> </tr> <tr> <td>$\text{Ru}_2\text{Os}(\text{CO})_{12}$</td> <td></td> <td></td> <td></td> </tr> </table>			Clusters	$\text{RuOs}_2(\text{CO})_{12}$	$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$	$\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$	Catalysis	$\text{H}_2\text{FeRu}_3(\text{CO})_{13}$	$\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$	Mixed-metal clusters	Water-Gas				$\text{Ru}_2\text{Os}(\text{CO})_{12}$			
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$\text{Ru}_2\text{Os}(\text{CO})_{12}$																		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ reacts with CO to liberate H_2 and produce $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$. A similar reaction occurs with $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ to form $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$, respectively. Since the tetranuclear clusters are readily separated by chromatography, this																		

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reaction affords an indirect means of separating $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$. The mechanistic implications of this reaction for the cluster catalyzed water-gas shift reaction are discussed

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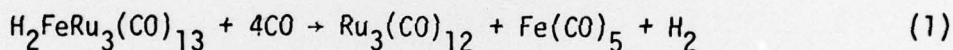
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Separation and Characterization of $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$.

Experiments Pertaining to the Mechanism of
the Cluster Catalyzed Water Gas Shift Reaction

Sir:

While enriching $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ for a ^{13}C DNMR study¹ by stirring the cluster under an atmosphere of ^{13}CO , we observed that a substantial amount of $\text{Ru}_3(\text{CO})_{12}$ was formed. Gas chromatographic and mass spectral analysis of the gases above the reaction mixture showed the presence of H_2 , and infrared spectroscopy confirmed the formation of $\text{Fe}(\text{CO})_5$. The overall reaction shown in eq. 1 was thus indicated.



Suspecting that this might be a general reaction, we subsequently examined the reactivity of several other tetranuclear mixed-metal clusters with CO. We report herein that reactions of this type afford a novel synthetic method for separating $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$, and we discuss the mechanistic implications of reaction 1 for the cluster catalyzed²⁻⁴ water gas shift reaction.

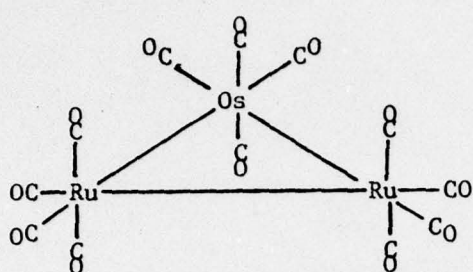
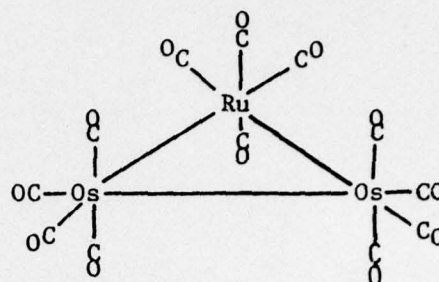
Johnson, Lewis and coworkers⁵ have reported that $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$ can be prepared by pyrolysis of an equimolar mixture of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ for 90 h at 175°C in xylene under a CO atmosphere. In our hands, this reaction produced a 1:2:2:1 mixture of Ru_3 , Ru_2Os -, RuOs_2 -, and $\text{Os}_3(\text{CO})_{12}$.^{6,7} We, and others,⁸ have found that this mixture of trimers is inseparable by normal chromatography and fractional crystallization techniques.⁹ However, the mixed-metal clusters H_2FeRu_2 -

$\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ can be synthesized from this trimer mixture and they are readily separated by chromatography on silica gel.^{6,7}

Reactions analogous to that in eq. 1 then afford a method for obtaining pure $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$.

A CH_2Cl_2 solution of pure $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ was allowed to stir at room temperature under a CO atmosphere for 16 days. Chromatography of this solution on silica gel yielded unreacted $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and yellow $\text{Ru}_2\text{Os}(\text{CO})_{12}$ (<5% yield) as the only detectable products. $\text{Fe}(\text{CO})_5$ was presumably formed in this reaction but was lost during solvent evaporation prior to chromatography. The analogous reaction of $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ with CO is not detectable at room temperature but proceeds slowly at 50°C to give isolable quantities of $\text{RuOs}_2(\text{CO})_{12}$ after 24 days. Thus, although $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$ cannot be directly separated, they can be isolated pure by first synthesizing and separating the tetranuclear clusters and then reacting these separately with CO.

The $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$ trimers have been characterized by their infrared and mass spectra and $\text{Ru}_2\text{Os}(\text{CO})_{12}$ by its ^{13}C NMR spectrum. Parent ions at 732 and 822 mass units with the correct isotopic distribution were respectively observed in the mass spectra, and each cluster showed fragments attributable to loss of 12 carbonyl ligands. The infrared spectra are shown in Figure 1 along with the spectra of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ for comparison. The overall similarity of the spectra indicates that the mixed metal trimers have the expected structures 1 and 2 analogous to $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$.

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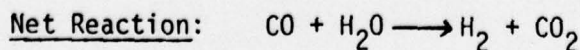
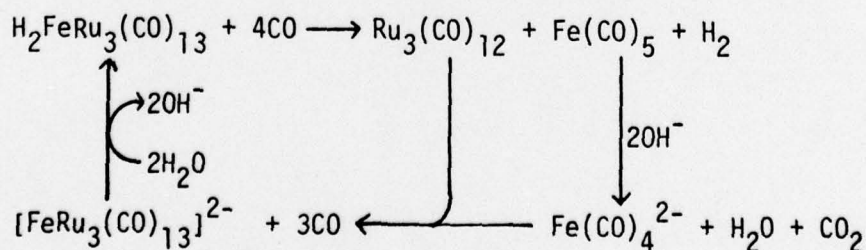
The ^{13}C NMR spectrum of $\text{Ru}_2\text{Os}(\text{CO})_{12}$ ¹⁰ at 25° C shows a sharp singlet at 192.2 ppm, indicative of rapidly exchanging carbonyl ligands. $\text{Ru}_3(\text{CO})_{12}$ (25°C) and $\text{Os}_3(\text{CO})_{12}$ (156°C) show corresponding singlets at 198.0 and 178.1 ppm.¹¹ A 2:1 weighting of the chemical shifts of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ gives a calculated value of 191.4 ppm for $\text{Ru}_2\text{Os}(\text{CO})_{12}$. The excellent agreement between the calculated (191.4) and experimentally observed (192.2) shifts illustrates the feasibility of using such additive relationships within an isostructural series. The exchange process of $\text{Ru}_2\text{Os}(\text{CO})_{12}$ can be slowed at low temperatures, and these results will be discussed in detail in a separate paper.

Reaction of this type of cluster with CO has been extended to $\text{H}_2\text{Ru}_4(\text{CO})_{13}$,¹² $\text{HCoRu}_3(\text{CO})_{13}$,¹³ $\text{HCoRu}_2\text{Os}(\text{CO})_{13}$,¹³ and $\text{HCoRuOs}_2(\text{CO})_{13}$.¹³ The reactivity is very dependent on the metals present. At room temperature $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$, and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ react slowly over a period of several days, whereas the reaction is complete within minutes for $\text{H}_2\text{Ru}_4(\text{CO})_{13}$, $\text{HCoRu}_3(\text{CO})_{13}$, $\text{HCoRu}_2\text{Os}(\text{CO})_{13}$, and $\text{HCoRuOs}_2(\text{CO})_{13}$.¹⁴ The reaction rate increases with increasing temperature and, for example, 90% of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ is converted to products after 90 h at 70°C. The rate of reaction is also solvent dependent. When conducted in a 15/1 mixture of 2-ethoxyethanol

and water, the polar solvent system used in the catalytic studies discussed below,^{2,3} the rate of the $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ reaction at 70°C increased at least 8-fold.¹⁵ The intimate details of this reaction remain obscure. However, the absence of Fe containing trimers and the lack of Ru-Os scrambling during formation of $\text{Ru}_2\text{Os}(\text{CO})_{12}$ and $\text{RuOs}_2(\text{CO})_{12}$ from $\text{H}_2\text{FeRu}_2\text{Os}(\text{CO})_{13}$ and $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$, respectively, indicates that this portion of the cluster remains intact throughout the conversion.¹⁶

Several carbonyl clusters have been demonstrated to catalyze the water gas shift reaction,²⁻⁴ and tetranuclear clusters have been implicated as key intermediates. Ford and coworkers^{2,3} have shown that the catalyst solutions prepared from $\text{Ru}_3(\text{CO})_{12}$ and OH^- contain predominately $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ and $[\text{HRu}_4(\text{CO})_{13}]^-$. The most active catalyst which Ford described³ was prepared from an $\text{Fe}(\text{CO})_5/\text{Ru}_3(\text{CO})_{12}$ mixture in alkaline solution, and infrared evidence indicated the formation of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ under these conditions. Subsequent experiments showed that the same high activity could be obtained by direct use of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ as the catalyst.³ The observations reported herein combined with our previous synthetic studies^{6,7} suggest a reasonable mechanism for the $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ catalyzed water gas shift reaction, Scheme I.

Scheme I



$\text{Fe}(\text{CO})_5$ is known to react with hydroxide to produce CO_2 and either $\text{Fe}(\text{CO})_4^{2-}$ or $\text{HFe}(\text{CO})_4^-$, depending on pH.^{4,17,18} We previously showed^{6,7} that $\text{Fe}(\text{CO})_4^{2-}$ reacts rapidly with $\text{Ru}_3(\text{CO})_{12}$ to produce the apparent intermediate $\text{FeRu}_3(\text{CO})_{13}^{2-}$ which gives $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ upon protonation. This particular reaction is quite rapid, giving an immediate color change upon combination of the reactants at room temperature and is essentially complete within 1 h. $[\text{HFe}(\text{CO})_4]^-$ also reacts with $\text{Ru}_3(\text{CO})_{12}$, albeit at a rate slower than $[\text{Fe}(\text{CO})_4]^{2-}$ to yield $\text{HFeRu}_3(\text{CO})_{13}^-$.¹⁹ The observation³ of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ in the $\text{Fe}(\text{CO})_5/\text{Ru}_3(\text{CO})_{12}$ catalyst solutions indicates that $\text{FeRu}_3(\text{CO})_{13}^{2-}$ and $\text{HFeRu}_3(\text{CO})_{13}^-$ are sufficiently strong bases to abstract H^+ from water.²⁰ Indeed, in the proposed mechanism one of the key functions of the cluster system is to provide a means for abstraction of hydrogen from water. Reaction of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ with CO subsequently liberates H_2 and produces $\text{Fe}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$. The relatively slow rate of the reaction of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ with CO suggests that this may be the rate limiting step in the overall catalytic cycle.

The strong experimental evidence which we have obtained for the various steps in the above mechanism does not of course preclude other mechanisms from operating. One of the key factors governing any mechanism is the solution pH. In the catalytic cycle discussed above, the solution must be basic enough to allow the $\text{Fe}(\text{CO})_5 \rightarrow \text{Fe}(\text{CO})_4^{2-}$ (or $\text{HFe}(\text{CO})_4^-$) reaction to occur yet sufficiently acidic to allow protonation of $\text{FeRu}_3(\text{CO})_{13}^{2-}$ (or $\text{HFeRu}_3(\text{CO})_{13}^-$).

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References and Notes

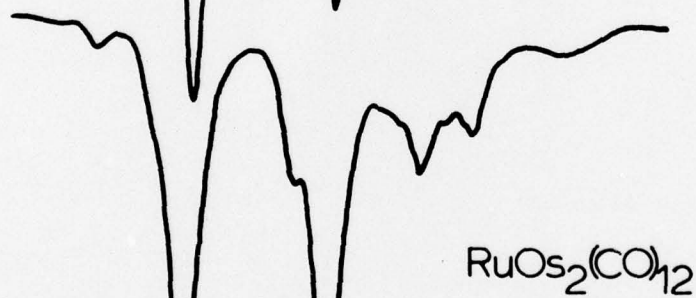
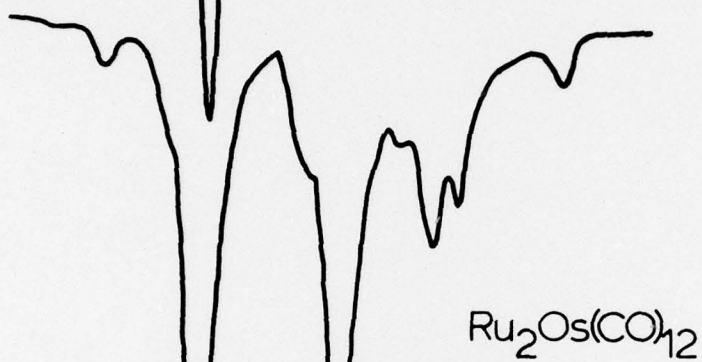
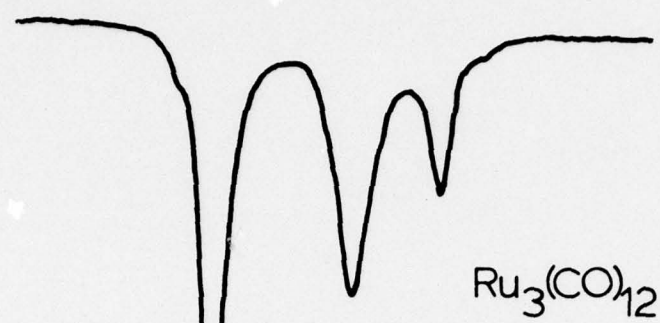
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14. Kaesz has observed a similar reactivity of $\text{H}_4\text{Re}_4(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ with CO. The former is unsaturated and reacts rapidly with CO at room temperature to produce $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and $\text{HRe}(\text{CO})_5$ [R. Saillant, G. Barcelo, and H. Kaesz, J. Am. Chem. Soc. **92**, 5739 (1970)]. Carbon monoxide converts $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ into $\text{Ru}_3(\text{CO})_{12}$, but the reaction conditions were not specified [H. D. Kaesz, Chem. Brit. **9**, 344 (1973)].
15. Without CO present, no $\text{Ru}_3(\text{CO})_{12}$ is found upon heating $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ in the 15/1 mixture of 2-ethoxyethanol and water. Rather, deprotonation occurred to generate $\text{HFeRu}_3(\text{CO})_{13}^-$ as the dominant solution species.

16. Preliminary analysis of the reactions of $\text{HCoRu}_2\text{Os}(\text{CO})_{13}$ and $\text{HCoRuOs}_2(\text{CO})_{13}$ with CO shows that Ru-Os scrambling does occur with these clusters and each gives a mixture of Ru-Os trimers in addition to other products. The formation of $\text{Ru}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$ was observed in the reaction of $\text{HCoRu}_3(\text{CO})_{13}$ with CO, but the Co containing products have not been conclusively identified. The $\text{Ru}(\text{CO})_5$ observed must arise directly from $\text{HCoRu}_3(\text{CO})_{13}$ rather than from $\text{Ru}_3(\text{CO})_{12}$ since the latter does not react with CO under these conditions.
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19. Reaction of $[\text{PPN}][\text{HFe}(\text{CO})_4]$ with $\text{Ru}_3(\text{CO})_{12}$ in refluxing THF was complete after 4 h. Removal of THF under vacuum followed by extraction of the residue with ether and crystallization from ether/hexane gave black crystals of $[\text{PPN}][\text{HFeRu}_3(\text{CO})_{13}]$. Anal. Calcd.: C, 46.60; H, 2.48. Found: C, 45.94; H, 2.57. ν_{CO} (CH_2Cl_2): 2073 w, 2031 s, 2013 s, 1998 s, 1974 m, 1944 m, 1840 w, 1811 m. Reaction of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ with KH [following the procedure of K. E. Inkrott and S. G. Shore, J. Am. Chem. Soc. **100**, 3954 (1978)] in THF for 24 h gave $[\text{K}][\text{HFeRu}_3(\text{CO})_{13}]$. ν_{CO} (THF): 2060 w, 2030 s, 2012 s, 1995 vs, 1969 m, 1945 sh, 1848 w, sh, 1823 m, 1780 w.
20. $[\text{K}][\text{HFeRu}_3(\text{CO})_{13}]$ ¹⁹ does indeed protonate in water upon heating. $[\text{K}][\text{HFeRu}_3(\text{CO})_{13}]$ was dissolved in distilled water and n-hexane added. The hexane layer remained colorless until the mixture was warmed to 50°C when the hexane layer slowly turned orange. Infrared and TLC analysis of the hexane solution showed the presence of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ with a small amount of $\text{Ru}_3(\text{CO})_{12}$.
21. Fellow of the Alfred P. Sloan Foundation, 1978-1980; Camille and Henry Dreyfus Foundation Teacher-Scholar, 1977-1982.

Figure Caption

Figure 1. Infrared spectra of $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}_2\text{Os}(\text{CO})_{12}$, $\text{RuOs}_2(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ in hexane solution.

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